

[54] **MULTI-ZONE METHOD FOR DEMETALLIZING AND DESULFURIZING CRUDE OIL OR ATMOSPHERIC RESIDUAL OIL**

[75] Inventors: **Ronald H. Wolk**, Lawrence Twp., Mercer County, N.J.; **Govanon Nongbri**, Levittown; **William C. Rovesti**, Newtown, both of Pa.

[73] Assignee: **Hydrocarbon Research, Inc.**, New York, N.Y.

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Related U.S. Application Data

[63] Continuation of Ser. No. 255,452, May 22, 1972, abandoned.

[52] U.S. Cl. **208/210; 208/213; 208/216; 208/251 H**

[51] Int. Cl. **C10g 23/02**

[58] Field of Search **208/210, 213, 216, 251 H, 208/58, 59, 211**

[56] **References Cited**

UNITED STATES PATENTS

3,322,666	5/1967	Beuther et al.	208/112
3,418,234	12/1968	Chervenak et al.	208/210
3,530,066	9/1970	Kuwata et al.	208/251 H
3,623,974	11/1971	Mounce et al.	208/59
3,725,251	4/1973	Albert et al.	208/210
3,788,973	1/1974	Wolk et al.	208/251 H
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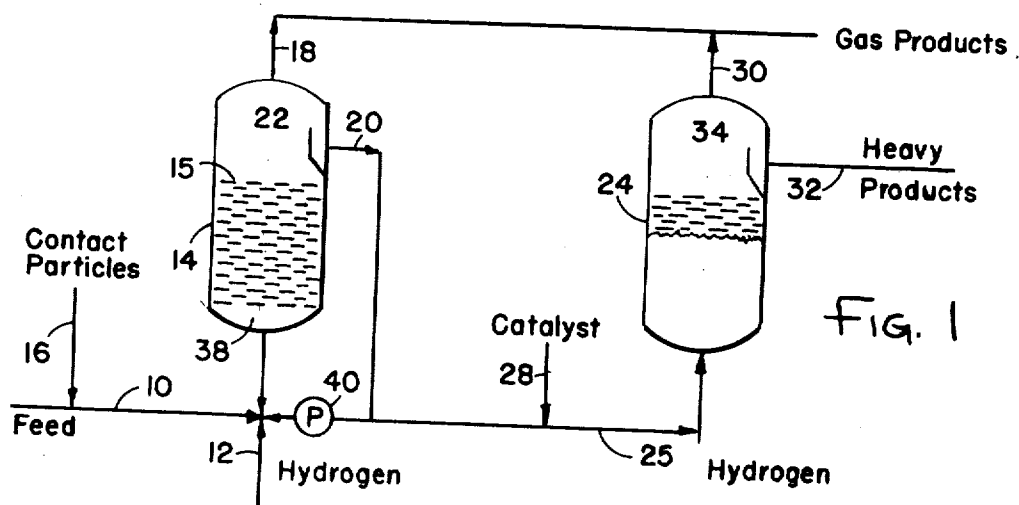
Primary Examiner—Delbert E. Gantz

Assistant Examiner—G. J. Crasanakis

[57] **ABSTRACT**

The high level desulfurization of petroleum residuums normally having at least 100 ppm of metals from the groups of vanadium and nickel is accomplished by an initial contact stage with a contact material such as Porocel, having extensive macroporosity with more than 0.15 cc/gram pore volume in pores greater than 125A in diameter operating as an ebullated bed under optimum demetallization conditions in the range of 730°–825°F (preferably 760°–780°F), and hydrogen partial pressure of 1000–2500 psi (preferably 1500–2000 psi), followed by a removal of effluent vapors and a further ebullated bed contact of the liquid with a highly active hydrodesulfurization catalyst which would ordinarily be rapidly poisoned by these residuums. By control of the first stage reaction conditions including space velocity, in the range of 0.20 to 1.5 volume of feed per hour per volume of reactor, and obtaining a high degree of demetallization in the order of 50–80% or more deposit of metals on the first stage contact particles, so that the amount of vanadium removed from the oil and taken up on the catalyst in the second stage was no more than 20 ppm, the life of the catalyst in the second stage was very greatly lengthened. The catalyst in the second stage has little macroporosity with no more than 0.10 cc/gram in pores greater than 125A in diameter so as to exclude most of the metal containing molecules which were not contacted in the first stage. This combination of the reaction steps makes it possible to achieve in excess of 75% desulfurization of these residuums.

4 Claims, 3 Drawing Figures



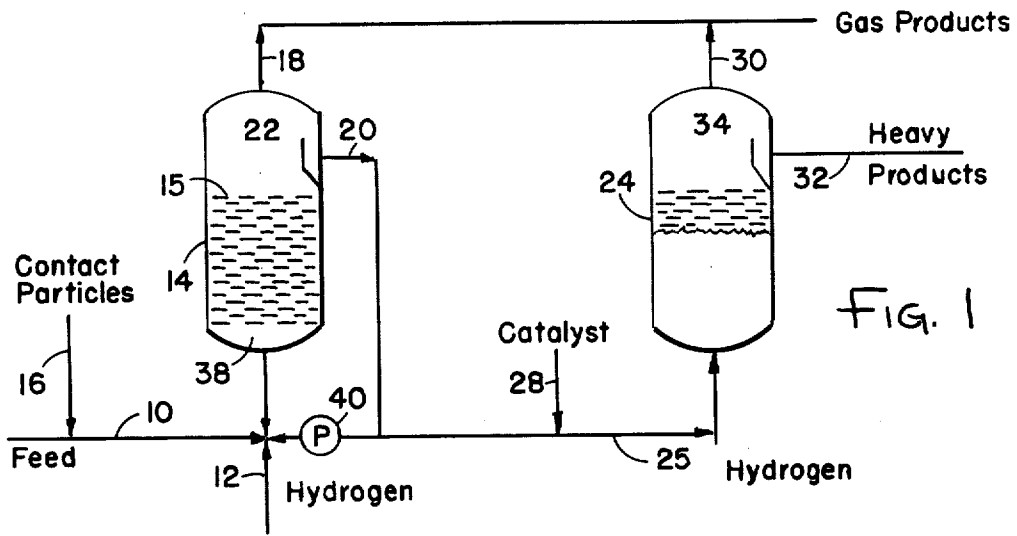


FIG. 1

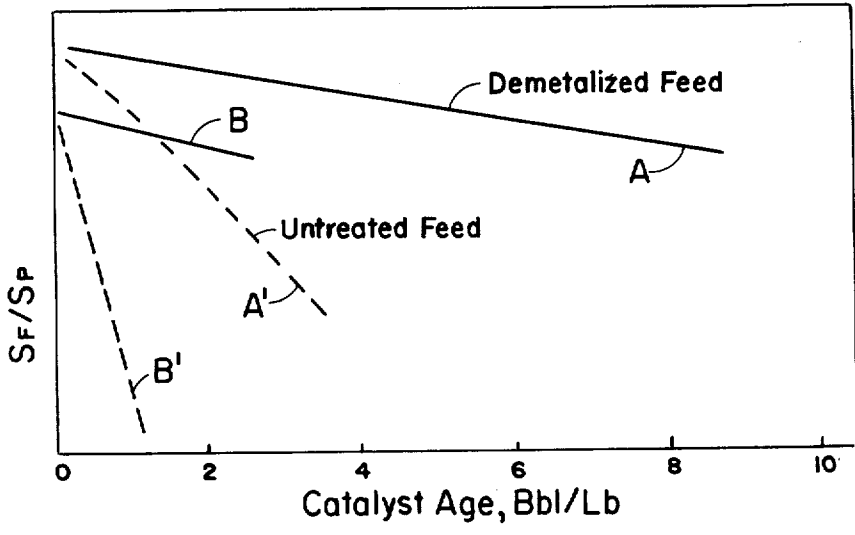


FIG. 2

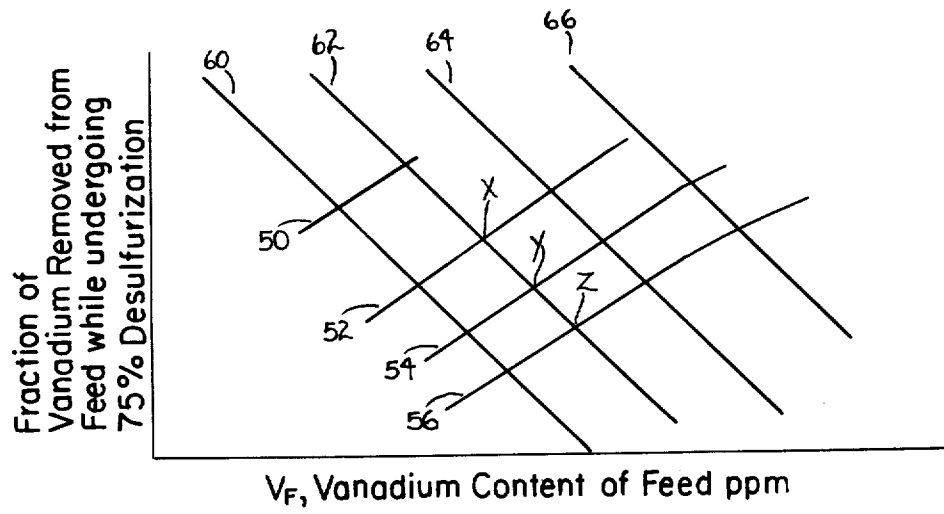


FIG. 3

MULTI-ZONE METHOD FOR DEMETALLIZING AND DESULFURIZING CRUDE OIL OR ATMOSPHERIC RESIDUAL OIL

This is a continuation of application Ser. No. 255,452, filed May 22, 1972 and now abandoned.

BACKGROUND OF THE INVENTION

The ebullated bed hydrodesulfurization of petroleum residuum is disclosed in the Chervenak et al. U.S. Pat. No. 3,418,234. It is also known that many residuum stocks contain substantial amounts of metals.

However, it has also been observed that in an ebullated bed hydrodesulfurization of a high metals containing residuum, the desulfurization catalyst was rapidly rendered inactive by the deposit of metals on and in the catalyst. This requires a frequent and expensive replacement of the catalyst which is otherwise expressed as low average catalyst life. Previous disclosures of two stage operations in which the second stage was a hydroconversion do not satisfactorily meet the requirements when the object is a desulfurization of high metals containing residuum in that the catalyst replacement cost for the first stage is too high. The maximum vanadium loading without severe activity loss on a catalyst is on the order of 0.3 lbs. vanadium per pound of fresh catalyst. This would be equivalent to limiting the catalyst life on a 400 ppm vanadium feed to less than 3 bbl/lb which is economically prohibitive.

SUMMARY OF THE INVENTION

It has now been determined that extremely long catalyst life can be obtained by careful maintenance of the metals content in the feed to a second stage catalyst desulfurization zone below a level in which the amount of vanadium that the second stage catalyst will remove is less than 20 ppm when obtaining desulfurization levels of 75% or more.

By selecting the pore size distribution of the first stage contact particles to be of a larger average size than the second stage catalyst then the vanadium containing molecules left after the first stage treatment are excluded from entering the pores of the second stage catalyst.

It appears that the vanadium compounds contained in the virgin residuum differ in character in terms of their ability to be removed from the oil. What is done is to take out most of the easily removed vanadium compounds and leave just a few of the more difficult to remove compounds in the feed to the catalytic stage. This reduces the poisoning rate in that catalytic stage to almost a trivial amount.

DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic view of a multiple stage hydrogeneration process.

FIG. 2 is a graph of sulfur removal against catalyst age for both virgin and demetallized light Venezuelan atmospheric residuum, and a graph of sulfur removal against catalyst age for both virgin and demetallized heavy Venezuelan atmospheric residuum.

FIG. 3 is a graph showing the amount of desulfurization as a function of the vanadium content of the feed.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the disclosed invention, a heavy

hydrocarbon charge such as a metals containing Venezuelan residuum at 10, together with hydrogen at 12 is introduced into a reactor 14 of the type shown in the U.S. Pat. No. 25,770. Such a reactor will be suitably charged with a demetallization contact material such as porous alumina, the particles being of an average size between about 60 mesh and 270 mesh. A small makeup of fresh contact particles is combined with the feed at 16. Alternately, contact particles in the form of extrudates of $\frac{1}{4}$ inch to $\frac{1}{32}$ inch diameter may be used, or granules of 10 to 60 mesh may be used.

The liquid and gas upflow through the bed of contact particles should be such that it will tend to expand the bed at least 10% based on the bed volume without fluid flow, and such that the particles are all in a random motion in the liquid. Such conditions are described as "ebullated" in the aforementioned Johanson patent.

Recycle of liquid effluent from above the contact particle interface 15 to below the distributor deck 38 is usually desirable to give proper temperature control and to establish a sufficient upflow velocity to assist in maintaining the particles in random motion in the case of particles in the form of $\frac{1}{32}$ to $\frac{1}{4}$ inch diameter extrudates. This recycle may be accomplished either externally utilizing pump 40, or internally as described in Johanson, supra.

Under the preferred conditions of temperature, pressure, throughput and product composition as hereinafter set forth, a vapor effluent is removed at 18 and a liquid effluent is removed at 20 from the upper portion 22 of the reaction zone 14. The liquid is then conducted to the second stage reactor 24.

In the second stage reactor the liquid feed at 20 joins with additional hydrogen at 26 and passes upwardly through a bed of desulfurization catalyst from the group of nickel, cobalt, molybdenum and tungsten on a carrier from the group of silica, alumina and mixtures thereof. Small amounts of desulfurization makeup catalyst may also be added at 28. A gaseous effluent is removed at 30, and a liquid is removed at 32 from the upper portion 34 of the reactor 24. The catalyst loading used in the second stage reactor 24 is about the same as that used for the contact particles in the first stage reactor 14.

EXAMPLE 1

Desulfurization of Demetallized Feeds

Catalyst Deactivation

Demetallized Light Venezuelan atmospheric resid (17.3°API, 2.09% S, 235 ppm V and 28 ppm Ni) was prepared by passing this feed over porous alumina having more than 0.15 cc/gram of pores greater than 125A in diameter, operating temperature was 760°F and hydrogen partial pressure was 2000 psi. Demetallized feed prepared in this manner was subsequently run over $\frac{1}{32}$ inch cobalt molybdate on alumina catalyst having a pore size distribution such that the pore volume in pores having a diameter greater than 125A is less than 0.10 cc/gram. The demetallized Light Venezuelan stock had an average metals content of about 55 ppm (40 ppm V and 15 ppm Ni).

Results of the desulfurization runs are presented in FIG. 2. The line A in FIG. 2 represents the deactivation curve for a high activity cobalt molybdate on alumina catalyst wherein the feed has been pretreated for demetallization while line A' represents the same high activity cobalt molybdate on alumina catalyst when un-

treated Light Venezuelan atmospheric resid was run. This catalyst contains 15.0% MoO₃, 3.5% CoO, has a bulk density of 50 lbs/ft³ and has less than 0.10 cc/gram pore volume in pores greater than 125A diameter.

The significant improvement in deactivation rate resulting from the use of the demetallized feed is apparent.

It is significant to note that the Ni and V loadings on the catalyst dump from the run in which demetallized Light Venezuelan atmospheric resid was run over 1/32 inch cobalt molybdenum extrudates where only 1.03 and 1.97 weight percent, respectively, on a fresh catalyst basis at catalyst age of 9.0 bbl/lb.

EXAMPLE 2

Demetallized Heavy Venezuelan atmospheric resid (12.6°API, 2.8% S, 375 ppm V and 57 ppm Ni) was prepared by passing this feed over porous alumina at 780°F and 2000 psi. The resulting demetallized feed, line B in FIG. 2, having a metals content of 139 ppm (104 ppm V and 35 ppm Ni) was run over 1/32 inch cobalt molybdate on alumina extrudates in order to compare the catalyst deactivation rate of this 139 ppm metals feed with the virgin feed line B'. Results of the two desulfurization runs over the same catalyst as used in Example 1 are presented in FIG. 2.

Despite the considerably higher metals level, the demetallized Heavy Venezuelan run up to an age of 2.75 B/lb showed no sign of rapid deactivation. Furthermore, the vanadium removed in this run was only about 18-22 ppm out of 104 ppm compared to 22 ppm out of 36 ppm in the case of Kuwait atmospheric resid over the same catalyst and at the same level of desulfurization.

This last observation is extremely important since it demonstrates that high metals-feeds need not be demetallized to the level of Kuwait atmospheric residuum (an economically prohibitive requirement in many cases) in order to effect a rate of vanadium deposition that will not rapidly deactivate a nonporous high activity desulfurization catalyst.

Table I presents data on the amount of demetallization that occurs when desulfurizing the residuums indicated to 75%. When desulfurizing the virgin feed about 60% demetallization occurs. However, if the feed is demetallized according to our invention before desulfur-

ization, then the amount of demetallization that occurs in the desulfurization step is a function of the vanadium content of the feed.

The graph of FIG. 3, on log-log scale, for the ordinate, shows the fraction of vanadium removed from the feed when undergoing a 75% desulfurization. The scale is from 0 to 1.0.

The abscissae is the vanadium content of the feed in parts per million to the desulfurization stage and the scale is from 0 to 1000.

Lines 50, 52, 54 and 56 represent experimental runs on feeds as follows:

50 is for a Kuwait atmospheric residuum originally having 36 ppm of vanadium after undergoing demetallization in the first stage.

52 is for a Khafji atmospheric residuum originally having 100 ppm of vanadium after undergoing demetallization in the first stage.

54 is for a Light Venezuelan atmospheric residuum originally having 200 ppm of vanadium after undergoing demetallization in the first stage.

56 is for a Heavy Venezuelan atmospheric residuum originally having 398 ppm of vanadium after undergoing demetallization in the first stage.

Lines 60, 62, 64 and 66 are mathematical calculations showing the parts per million of vanadium removed from the feed in the second or desulfurization stage as follows:

60 shows 10 ppm vanadium removal.

62 shows 20 ppm vanadium removal.

64 shows 40 ppm vanadium removal.

66 shows 100 ppm vanadium removal.

It is thus possible to determine the extent of demetallization in the first stage necessary to permit second stage demetallization at the 75% rate without depositing more than 20 ppm of vanadium on the catalyst.

For example, it would be necessary to demetallize Heavy Venezuelan atmospheric residuum from 398 ppm to 92 ppm vanadium (Point Z) in a demetallization step in order not to exceed 20 ppm of vanadium deposition on the desulfurization stage catalyst. Analogous values would be 72 for Light Venezuelan atmospheric (Point Y), 53 for Khafji atmospheric residuum (Point X) and 34 Kuwait atmospheric residuum. Since the value for Kuwait atmospheric residuum is so close to the feed value of 36 ppm, it would not be practical to put in a demetallization step for this feed.

TABLE I

Feed	Vanadium Content	% Vanadium Removal When Undergoing 75% Desulfurization
Virgin Heavy Venezuelan A.B.	400 ppm	45.5
Demetallized "	172	32.6
" "	104	28.8
Virgin Light Venezuelan A.B.	200	60.0
Demetallized "	98	26.1
" "	56	32.1
" "	42	16.6
Virgin Khafji A.B.	100	61.0
Virgin Kuwait A.B.	36	61.3
A.B. — Atmospheric Bottoms		
The preferred operating conditions for the two stages are:		
	1st	2nd
Temperature °F	730 - 825	700 - 800
Preferred	760 - 780	720 - 760
Hydrogen Partial Pressure (psi)	1000 - 2500	1000 - 2500
Preferred	1500 - 2000	1500 - 2000
Space Velocity V _g /hr/V _c	0.20 - 1.5	0.3 - 1.5
Preferred	0.3 - 0.9	0.5 - 1.0

While we have shown and described a preferred form of embodiment of our invention, we are aware that modifications may be made thereto within the scope and spirit of the description herein and of the claims appended hereinafter.

We claim:

1. A multi-zone method for desulfurizing a crude petroleum charge or atmospheric residual charge containing at least 100 ppm of metals from the group consisting of vanadium and nickel wherein said charge, in liquid phase, is passed upwardly with hydrogen-rich gas through a first reaction zone containing a particulate contact material and the effluent from said first reaction zone is then passed with hydrogen-rich gas upwardly through a second reaction zone containing a particulate hydrodesulfurization catalyst; under conditions in which said contact material and said hydrodesulfurization catalyst are maintained in random motion in the liquid, and wherein the temperature in said first reaction zone is maintained in the range of 730° to 825°F and the hydrogen partial pressure is in the range of 1000-2500 psi and space velocity in the order of 0.2-1.5 volume of feed/hr/volume of reaction zone, the improvement which comprises:

a. maintaining porous alumina as said contact material in said first reaction zone, said alumina having a pore volume of more than 0.15 cc/gram of pores having a diameter in excess of 125A;

b. maintaining reaction conditions in said second reaction zone substantially at the same pressure as in said first reaction zone with a maximum hydrogen rate of 5000 SCF/barrel, the temperature being between 700° and 800°F, the space velocity being between 0.3 and 1.5 volume of feed/hour/volume of reaction space wherein no more than 20 ppm of vanadium is removed in said second zone while a desulfurization of at least 75 percent is achieved in said second zone, said catalyst in said second reaction zone comprising a Group VI-B metal and iron group metal on alumina, said catalyst having a pore structure with less than 0.10 cc/gram in pores larger than 125A.

2. The method as claimed in claim 1 wherein said atmospheric residual charge is a heavy Venezuelan atmospheric bottoms containing in the order of 400 ppm of metals and the first stage operation is conducted under conditions to remove approximately 75% of the metals.

3. The method as claimed in claim 1 wherein said atmospheric residual charge is a light Venezuelan atmospheric bottoms containing in the order of 200 ppm of metals and the first stage operation is conducted under conditions to remove approximately 70% of the metals.

4. The method as claimed in claim 1 wherein said atmospheric residual charge is a Khafji atmospheric bottoms having in the order of 100 ppm of metals and the first stage operation is conducted under conditions to remove approximately 60% of the metals.

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